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(54) Title: SILICON OXIDE SLURRY AND METHOD FOR PRODUCING SUCH SLURRY

(57) Abstract: The present invention relates to a slurry containing water, amorphous silica particles having a particle size less than 1 µm and silica flour with a particle size between 2 - 200 µm. In order to stabilize the slurry, the slurry contains a polysaccharide. The invention further relates to a method for the production of a slurry containing water, amorphous silica having a particle size below 1 µm, and silica flour with a particle size between 2 - 200 µm, where a polysaccharide is added to a slurry of water and amorphous silica, whereafter the silica flour is mixed into the slurry of amorphous silica.

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**Title of invention**

Silicon oxide slurry and method for producing such slurry.

**Field of invention**

- 5 The present invention relates to an additive for oil well cement containing amorphous silica particles and silica flour and to a method for producing such additive

**Background art**

- 10 From EP-B 467921 it is known a method for the mixture of silicon dioxide to a hydraulic cement slurry, where amorphous silica with particles smaller than 1  $\mu\text{m}$  is mixed with water to form an aqueous slurry of microsilica whereafter silica flour with particles with a size from 2 – 200  $\mu\text{m}$  are mixed into the suspension of amorphous silica particles. Finally, the produced liquid slurry is added to a cement slurry in a mixing tank.

- 15 The cement slurry produced according to the method of EP-B 467921 is particularly useful for cementing oil wells at high temperatures of above 100°C as it has been found that this prevent long time reduction of strength of the cement.

- 20 In order to make full economic and practical use of the method according to EP-B 467921 the slurry containing amorphous silica and silica flour should be produced and transported to the cementing site for mixing to the cement slurry shortly before cementing. For use in cementing of oil wells offshore and on shore, this means that the slurry of microsilica and silica flour must be produced ashore and transported to a rig before it can be mixed into a cement
- 25 slurry. Unfortunately it has been found that the suspension of amorphous silica and silica flour shows a strong tendency of settling resulting in such a short shelf life that the suspension cannot be transported for mixing into cement slurries. There is thus a need for a slurry of the type disclosed in EP-B 467921 which have a reduced tendency of settling and which is compatible
- 30 with cement slurries.

### Disclosure of Invention

By the present invention it has now been provided a slurry of amorphous silica and silica flour and a method for production of such slurry which shows a strongly reduced tendency of settling and which is compatible with cement slurries and which does not contain any toxic additives.

Thus, according to a first aspect, the present invention relates to a slurry containing water, amorphous silica particles having a particle size less than 1 micrometer and silica flour having a particle size between 2 and 200  $\mu\text{m}$ , which slurry is characterized in that it contains a polysaccharide.

According to a preferred embodiment the polysaccharide is a cellulose derivate selected among xanthan, carboxymethylcellulose, hydroxymethylcellulose, hydroxyethylcellulose or mixtures of these compounds.

According to a further preferred embodiment the slurry contains between 0.01 and 3 grams of polysaccharide pr. litre of slurry and more preferably between 0.05 and 1.5 grams of polysaccharide pr. litre of slurry.

The amount of polysaccharide pr. litre of slurry is adjusted according to the chain length of the polysaccharide. When using polysaccharides having a short chain length, the amount of polysaccharide in the slurry is in the upper end of the ranges and when using polysaccharide having a long chain length the amount is in the lower part of the range.

In order to further increase the stabilizing effect of the polysaccharide, the slurry optionally contains one or more of dextrin, guar gum and locust bean gum.

The slurry according to the invention may contain varying amounts of amorphous silica and silica flour, but the amount of amorphous silica is generally between 15 - 50 % by weight based on the weight of the slurry and the amount of silica flour is generally between 5 and 60 % by weight based on the weight of the slurry.

The total amount of dry matter in the slurry is preferably between 40 and 80 % by weight based on the weight of the slurry.

It has surprisingly been found that the slurry according to the invention is very stable and shows little or no tendency of settling even after two to three months storage. The slurry can thus be stored and transported to the sites where it is mixed into cement slurries. Further it has been found that the slurry according to the invention is compatible with cement slurries in that it gives an acceptable rheology of the cement slurries.

According to a second embodiment the present invention relates to a method for the production of a slurry containing water, amorphous silica having a particle size below 1  $\mu\text{m}$ , and silica flour having a particle size between 2 and 200  $\mu\text{m}$ , which method is characterized in that a polysaccharide is added to a slurry of water and amorphous silica, whereafter the silica flour is mixed into the slurry of amorphous silica.

According to a preferred embodiment the polysaccharide is preconditioned in a water-containing medium for at least 15 minutes before it is added to the slurry of water and amorphous silica.

The polysaccharide is preferably preconditioned in a slurry of water and amorphous silica.

According to a preferred embodiment the polysaccharide added to the slurry of amorphous silica and water is a cellulose derivate such xanthan, carboxymethylcellulose, hydroxymethylcellulose, hydroxyethylcellulose or mixtures of these compounds.

Preferably the silica flour is mixed into the slurry of water and amorphous silica using a high shear energy mixer.

The polysaccharide is preferably added to the slurry of amorphous silica and water in an amount necessary to provide a content of polysaccharide in the final slurry of 0.01 to 3 grams pr. litre and more preferably in an amount of 0.05 and 1,5 grams pr litre.

It has surprisingly been found that the addition polysaccharide to the slurry of amorphous silica and silica flour results in a stable slurry with a strongly reduced tendency of settling resulting in a strongly increased shelf life of the slurries. The preconditioning of the polysaccharide has shown to even further  
5 improve the stability of the final slurry. Further it has been found that the addition of polysaccharides gives acceptable rheological properties for oil well cement slurries containing the slurries according to the invention. Finally polysaccharides are generally non-toxic compounds which are approved to be used in connection with oil well cements.

## 10 Detailed description of the Invention

### Example 1

0,44 grams of xanthan pr. litre of final slurry was added to a slurry of amorphous silica and water containing 50 % by weight of amorphous silica.  
15 The xanthan had been preconditioned in a small part of the slurry of water and amorphous silica for 24 hours before it was added. 850 grams pr litre of final slurry of silica flour having a mean particle size of 25  $\mu\text{m}$  was thereafter added to the slurry using a high shear mixer. The final slurry was stored in 100 ml glass cylinders for 34 days. The samples in the glass cylinders had a 2 mm  
20 top layer of water after 34 days, but no resistance was found when lowering a rod to the bottom of the cylinder. The samples were very fluid and when the cylinders were emptied there was not found and settling in the bottom of the cylinders.

For comparison purposes an identical slurry was made, but without the  
25 addition of xanthan. After 7 days it was found that excessive settling had occurred. The cylinder had a 25 mm top layer of water and a hard layer was found in the bottom of cylinder which layer could not be redispersed. The hard layer consisted of silica flour.

### Example 2

30 A slurry according to the invention was made in the same way as described in Example 1, except that 0.22 grams of hydroxyethylcellulose was added

instead of xanthan. The slurry was filled into a glass cylinder. After 1 week storage the slurry had a 10 mm top layer of water and no hard bottom layer was found.

### Example 3

- 5 A slurry according to the invention was made in the same way as described in Example 1, except that 0.22 grams carboxymethylcellulose was added instead of xanthan. The slurry was filled into a glass cylinder. After 1 week storage the slurry had a 8 mm top layer of water and no hard bottom layer was found.
- 10 The above examples show that the slurry according to the invention has a strongly reduced settling compared to the prior art slurry.

### Example 4

- A slurry of amorphous silica and silica flour containing xanthan according to the present invention and made according to Example 1 was added to an oil  
15 well cement slurry in an amount necessary to provide a total SiO<sub>2</sub> content in the cement slurry of 35 % by weight based on the weight of cement. The slurry had a density of 1.9 g/cm<sup>3</sup>. This slurry is denoted slurry A

- For comparison purpose it was made an identical cement slurry B except that cement slurry B was made by adding a slurry of amorphous silica and silica  
20 flour that did not contain a polysaccharide additive.

The rheological properties of the two cement slurries were measured according to API Specification 10 and the results are shown in Table 1.

**TABLE 1**

<b>Cement slurry</b>	<b>A</b>	<b>B</b>
Rheology (20°C)		
Plastic viscosity, cp	64.5	48
Yield point, lb/100ft <sup>3</sup>	8.5	3
Rheology (88°C)		
Plastic viscosity, cp	45	37.5
Yield point, lb/100ft <sup>3</sup>	6	1.5

- 5 As can be seen from Table 1, the rheological properties of a cement slurry containing the slurry of amorphous silica and silica flour according to the invention does not deviate much from the same properties of the prior art slurry B and are well within the ranges accepted for oil well cement slurries.

**CLAIMS:**

1. Slurry containing water, amorphous silica particles having a particle  
5 size less than 1  $\mu\text{m}$  and silica flour with a particle size between 2 – 200  $\mu\text{m}$ ,  
c h a r a c t e r i z e d i n that the slurry contains a polysaccharide as a  
stabilizer.
2. Slurry according to claim 1, c h a r a c t e r i z e d i n that the  
polysaccharide is a cellulose derivate selected among xanthan,  
10 carboxymethylcellulose, hydroxymethylcellulose, hydroxyethylcellulose and  
mixtures of these compounds.
3. Slurry according to claim 1, c h a r a c t e r i z e d i n that the slurry  
contains between 0.01 and 3 grams of polysaccharide pr. litre of slurry.
- 15 4. Slurry according to claim 3, c h a r a c t e r i z e d i n that the slurry  
contains between 0.05 and 1.5 grams of polysaccharide pr. litre of slurry.
5. Slurry according to claim 1 – 4, c h a r a c t e r i z e d i n that the  
slurry further contains one or more of dextrin, guar gum and locust bean gum.
6. Method for the production of a slurry containing water, amorphous  
20 silica having a particle size below 1  $\mu\text{m}$ , and silica flour with a particle size  
between 2 – 200  $\mu\text{m}$ , c h a r a c t e r i z e d i n that a polysaccharide is  
added to a slurry of water and amorphous silica, whereafter the silica flour is  
mixed into the slurry of amorphous silica.
7. Method according to claim 6, c h a r a c t e r i z e d i n that the  
25 polysaccharide is preconditioned in a water containing medium.
8. Method according to claim 7, c h a r a c t e r i z e d i n that  
polysaccharide is preconditioned in a slurry of water and amorphous silica.



9. Method according to claim 6, characterized in that the silica flour is mixed into the slurry of water and amorphous silica using a high shear energy mixer.
10. Method according to claim 6, characterized in that the polysaccharide is added to the slurry of amorphous silica and water in an amount necessary to provide a content of polysaccharide in the final slurry of 0.01 to 3 grams pr. litre.
11. Method according to claim 10, characterized in that the polysaccharide added to the slurry of amorphous silica and water in an amount necessary to provide a content of polysaccharide in the final slurry of 0.1 and 1,5 grams pr litre.
12. Method according to claim 1 -10, characterized in that the polysaccharide added is a cellulose derivate selected among xanthan, carboxymethylcellulose, hydroxymethylcellulose, hydroxyethylcellulose and mixtures of these compounds.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO 03/00135

## A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C04B 24/38, C04B 22/06

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-INTERNAL

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 9011977 A1 (DEN NORSKE STATS OLJESELSKAP A.S.), 18 October 1990 (18.10.90), page 5, line 1 - line 24; page 7, line 23 - page 8, line 21 --	1-5,6-12
X	DE 4106380 A1 (SANDOZ-PATENT-GMBH), 5 Sept 1991 (05.09.91), column 1, line 31 - line 45; column 2, line 18 - line 32 --	1-5,6-12
A	EP 1078897 A1 (HALLIBURTON ENERGY SERVICES, INC.), 28 February 2001 (28.02.01), page 4, line 5 - line 36 --	1-5,6-12

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

\* Special categories of cited documents:

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"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

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## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2002/0059885 A1 (EVELYNE PRAT ET AL), 23 May 2002 (23.05.02), paragraph 0059; paragraph 0067 ---	1-5,6-12
A	US 5356671 A (JOSEF F. DRS), 18 October 1994 (18.10.94), column 1, line 41 - line 49; column 2, line 14 - line 46 -- -----	1-5,6-12

# INTERNATIONAL SEARCH REPORT

Information on patent family members

26/07/03

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Patent document cited in search report				Publication date		Patent family member(s)		Publication date	
WO	9011977	A1	18/10/90	AT	107612	T		15/07/94	
				AU	627871	B		03/09/92	
				AU	5415590	A		05/11/90	
				BR	9007277	A		24/03/92	
				CA	2050594	A,C		11/10/90	
				DE	69010196	D		00/00/00	
				DK	467921	T		01/08/94	
				EP	0467921	A,B		29/01/92	
				NO	167649	B,C		19/08/91	
				NO	891463	A		11/10/90	
				RU	2078741	C		10/05/97	
-----									
DE	4106380	A1	05/09/91	AT	45791	A		15/06/94	
				AT	398756	B		25/01/95	
				AU	637676	B		03/06/93	
				AU	7202991	A		05/09/91	
				BE	1005315	A		29/06/93	
				CA	2037303	A		04/09/91	
				CH	681541	A		15/04/93	
				ES	2027933	A		16/06/92	
				FR	2659959	A,B		27/09/91	
				GB	2241499	A,B		04/09/91	
				GB	9104082	D		00/00/00	
				HK	148996	A		16/08/96	
				IT	1244656	B		08/08/94	
				IT	RM910146	D		00/00/00	
				JP	5254907	A		05/10/93	
				NO	309141	B		18/12/00	
				NO	910816	A		04/09/91	
				SE	9100602	A		04/09/91	
				US	5356671	A		18/10/94	
-----									
EP	1078897	A1	28/02/01	CA	2316711	A		26/02/01	
				DE	60003126	D		00/00/00	
				NO	20004265	A		27/02/01	
				US	6478868	B		12/11/02	
-----									
US	2002/0059885	A1	23/05/02	NONE					
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**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

26/07/03

International application No.

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Patent document cited in search report			Publication date	Patent family member(s)		Publication date
US	5356671	A	18/10/94	AT	45791 A	15/06/94
				AT	398756 B	25/01/95
				AU	637676 B	03/06/93
				AU	7202991 A	05/09/91
				BE	1005315 A	29/06/93
				CA	2037303 A	04/09/91
				CH	681541 A	15/04/93
				DE	4106380 A	05/09/91
				ES	2027933 A	16/06/92
				FR	2659959 A,B	27/09/91
				GB	2241499 A,B	04/09/91
				GB	9104082 D	00/00/00
				HK	148996 A	16/08/96
				IT	1244656 B	08/08/94
				IT	RM910146 D	00/00/00
				JP	5254907 A	05/10/93
				NO	309141 B	18/12/00
				NO	910816 A	04/09/91
				SE	9100602 A	04/09/91

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